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(21) International Application Number: PCT/US94/14658 (22) International Filing Date: 14 December 1994 (14.12.94) (30) Priority Data: 08/166,552 14 December 1993 (14.12.93) US (71) Applicant: THE TRUSTEES OF THE UNIVERSITY OF PENNSYLVANIA [US/US]; Center for Technology Transfer, Suite 300, 3700 Market Street, Philadelphia, PA 19104-3147 (US). (72) Inventors: SWAGER, Timothy, M.; 1301 Wyngate Road, Wynnewood, PA 19096 (US). MARSELLA, Michael, J.; 628 South 19th Street, Philadelphia, PA 19104 (US). (74) Agents: ELDERKIN, Dianne, B. et al.; Woodcock Washburn Kurtz Mackiewicz & Norris, 46th floor - One Liberty Place, Philadelphia, PA 19103 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: DERIVATIZED POLYTHIOPHENES AND DEVICES COMPRISING SAME (57) Abstract Novel polythiophene derivatives are provided along with sensing devices comprising such derivatives in a layer disposed upon a substrate. In preferred embodiments, the polythiophene derivatives bear crown ether moieties covalently bound to 3 positions of adjacent thiophene units.		

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DERIVATIZED POLYTHIOPHENES AND DEVICES COMPRISING SAME**GOVERNMENT SUPPORT**

This work has been supported by National Science Foundation Grant DMR-9258298 and DMR-9120668.

5 FIELD OF THE INVENTION

This invention relates to materials that are useful in the fabrication of chemical sensing devices. This invention also relates to methodologies whereby organic compounds are derivitized to find use in such devices. In one preferred
10 embodiment, the invention relates to crown ether-containing polythiophenes that exhibit ion-selective chemical sensitivity.

BACKGROUND OF THE INVENTION

The concentrations of metal ions in various media are extensively measured both in the biological sciences and in the
15 health care industry. Several methodologies exist for taking these measurements, including the use of ion selective electrodes, ion responsive dyes, and ion sensitive field effect transistors (IFETS). (See, e.g., Supramolecular Chemistry I - Directed Synthesis and Molecular Recognition, Weber, E., Ed.,
20 Springer-Verlag, New York, 1993.) However, ion selective electrodes have the disadvantage that they are not easily miniaturized, and IFETS and ion responsive dyes lack the high sensitivity necessary for trace analysis.

Conducting polymers (CPs) have been the focus of
25 considerable interest because they combine the relatively low cost and ease of manufacturing of polymers with the conductive properties of metals and semiconductors. Moreover, the

conductivity of conducting polymers is highly responsive to both conformational and electrostatic perturbations. For example, it is well known that twisting a conducting polymer's backbone from planarity can result in a conductivity drop as high as 10^5 or greater. See, e.g., Handbook of Conducting Polymers, Skotheim, T.J., Ed., Dekker, New York, 1986. Hence, conductivity changes in conducting polymers provide a large dynamic range which, if harnessed effectively, can result in very sensitive sensory materials. Such conductivity changes easily can be monitored and miniaturized. See, e.g., Kittlesen, et al., *J. Am. Chem. Soc.* 1984, 106, 7389.

Conducting polymer-based sensors have been previously reported. (See, e.g., Thackeray, et al., *J. Phys. Chem.* 1986, 90, 6674; Zotti, *Synthetic Metals* 1992, 51, 373.) However, known polymer-based sensors are chemically irreversible and cannot detect a time dependent signal in real time. This is a serious deficiency where it is desired to measure stimuli which vary over time, such as in the monitoring of electrolyte concentrations in bodily fluids. Additionally, there are no systems at present that can be easily modified to detect a variety of chemical species.

Substituted polythiophenes are an ideal choice for sensory materials due to their ease of structural modifications, high conductivity, and environmental stability. In addition, recent studies have shown the conductivity of these materials to be highly sensitive to the nature and regiospecificity of covalently bound sidechains, indicating that small conformational changes produce large effects. (See, e.g., Roncali, *J. Chem. Rev.* 1992, 92, 711; Heywang, et al., *Adv. Mater.* 1992, 4, 116; McCullough, et al., *J. Am. Chem. Soc.* 1993, 115, 4910.) However, previous attempts to develop polythiophene-based sensory materials showed no ion-selective electrochemical response. (see, Sable, et al., *Electrochimica Acta* 1991, 36, 15.)

Consequently, there remains a need in the art for conductive polymers whose conductivities change reversibly in response to a variety of chemical species.

OBJECTS OF THE INVENTION

It is one object of the present invention to provide novel, conductive polythiophenes.

It is another object of the invention to provide
5 derivatized polythiophenes whose conductivities change
measurably and selectively in response to metal ions and other
chemical species.

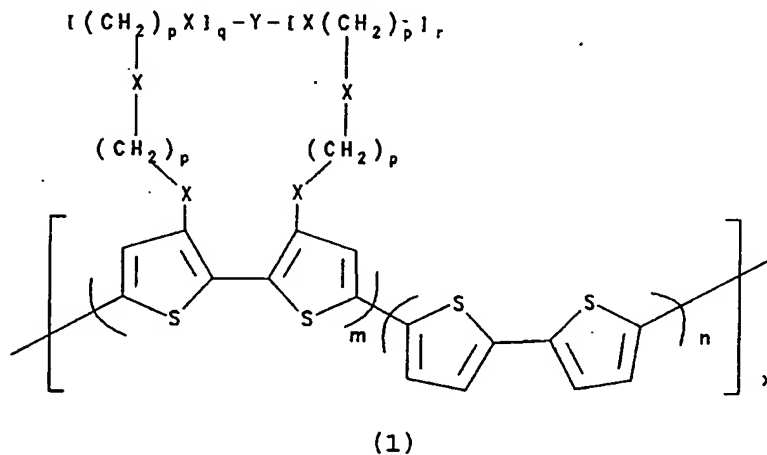
It is a further object to provide materials that include such derivatized polythiophenes.

10 It is yet another object to provide sensing devices
that include such materials.

SUMMARY OF THE INVENTION

These and other objects are satisfied by the present invention, which provides novel polythiophene derivatives and
15 sensing devices containing such derivatives.

In certain embodiments, the polythiophene derivatives have formula (1):



wherein:

each X is O, NR₃, or S;

20 R₃ is alkyl having 1 to about 5 carbon atoms;

Y is $(\text{CH}_2)_p$, aryl having 6 to about 14 carbon atoms, or calixarenyl having 18 to about 200 carbon atoms;

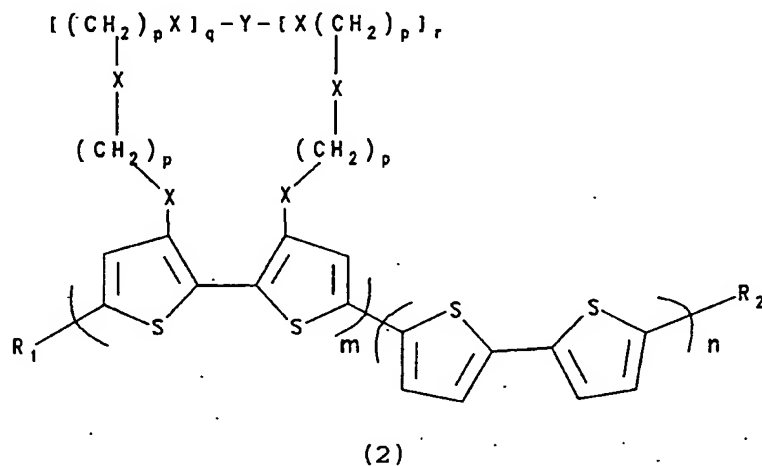
m is 1 to about 5;

n is 0 to about 5;
each p is, independently, 1 to about 5;
each q is, independently, 0 to about 5; and
x is 1 to about 1000.

5 In preferred embodiments, each X is O, Y is $(CH_2)_2$, n is 0 or 1, m is 1, each p is 2, q is 1, r is 0, and x is 1 to about 10.

In another aspect, the invention provides compounds that find use in preparing such derivatized polythiophenes. In one embodiment, the invention provides compounds having formula

10 (2) :



wherein R_1 and R_2 are, independently, H, Cl, Br, I, Li, $Sn(R_3)_3$, or $Si(R_3)_3$, n is 0 or 1, and m is 1.

The present invention further provides sensing devices that include novel polythiophene derivatives. In general, the devices comprise a layer that contains at least one polythiophene derivative of the invention disposed upon a substrate. The layer can contain the derivative in pure or substantially pure form or in combination with other chemical compounds such as known synthetic organic polymers.

20 The invention also provides methods for preparing sensors comprising the steps of providing a substrate and placing upon said substrate at least one layer that includes at least one polythiophene derivative according to the invention.

Also provided are methods for using the sensors of the
25 invention, comprising contacting the polythiophene containing

layer to a chemical species and then determining any resulting change in conductivity for the polythiophene.

BRIEF DESCRIPTION OF THE DRAWINGS

The numerous objects and advantages of the present invention may be better understood by those skilled in the art by reference to the accompanying figures, in which:

Figure 1 shows the reversible manner in which compounds of the invention bind metal ions.

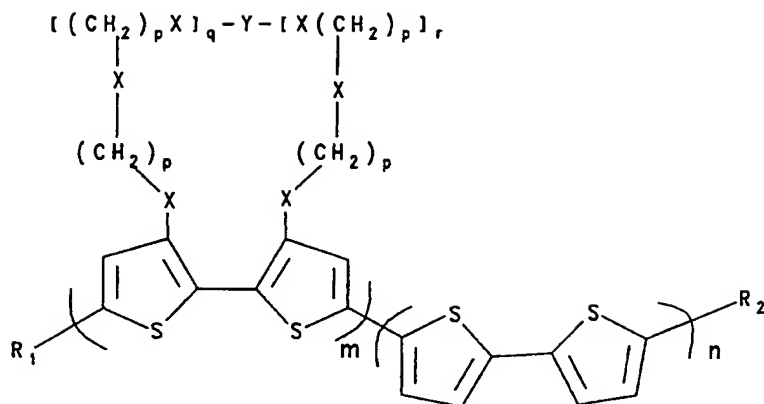
Figure 2 shows a sensing device according to the invention.

Figure 3 shows exemplary synthetic routes according to the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention provides new compounds and sensing devices useful in the detection of a variety of chemical species. In preferred embodiments, the detected species is an ion, that is, a chemical moiety that bears a net positive or net negative electrical charge. Preferred ions for detection are metal ions, particularly ions of metals belonging to Groups I and II of the Periodic Table. Particularly preferred are calcium ions, magnesium ions, and ions of the alkali metals (i.e., lithium, potassium, sodium, cesium, and rubidium).

According to one embodiment of the invention, somewhat monomeric bithiophene compounds are provided having the formula (2):

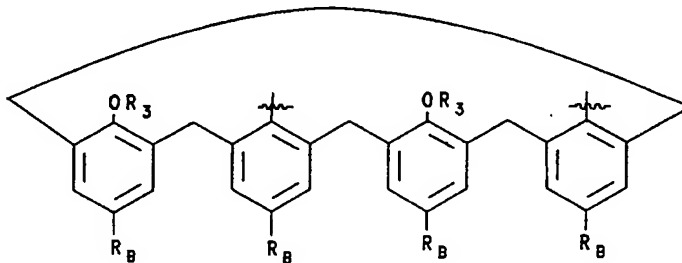


(2)

Each X can be independently selected to be O, NR₃, or S wherein R₃ is alkyl having 1 to about 5 carbon atoms. The term alkyl is intended to denote both straight chain and branched hydrocarbon moieties such as methyl (CH₃), methylene (CH₂), and ethyl (CH₂CH₃) groups. X preferably is O.

Y can be $(CH_2)_p$, aryl having 6 to about 14 carbon atoms, or calixarenyl having 18 to about 200 carbon atoms; . The term aryl is intended to denote monocyclic and polycyclic aromatic groups including, for example, phenyl, naphthyl, benzyl, and xyl groups and substituted derivatives thereof. Y preferably is $(CH_2)_2$ or phenyl. Additionally, the aryl portion of Y can be substituted at one or more positions to afford additional degrees of selectivity and specificity in the binding of a chemical species. The term calixarenyl is intended to denote polycyclic groups derived from one or more calixarenes. A wide variety of functionalized calixarenes suitable for use in accordance with the invention are known in the art, as are methods for their preparation. Indeed, the organic chemistry of calixarenes is extensive (see, e.g., Gutsche, *Calixarenes*, Royal Society of Chemistry (1989); *Calixarenes: A Versatile Class of Macroscopic Compounds*, Vicens and Klewer, eds., Academic Publishers (1991); Cram, *Science* 1983, 219, 1177). A number of calixarene derivatives are disclosed in United States Patent Application Serial. No. 08/011,301, filed January 29, 1993, which is incorporated

herein by reference. One representative calixarenyl group according to the invention has formula (3) wherein R_B is H or a group that is electron-withdrawing relative to hydrogen.

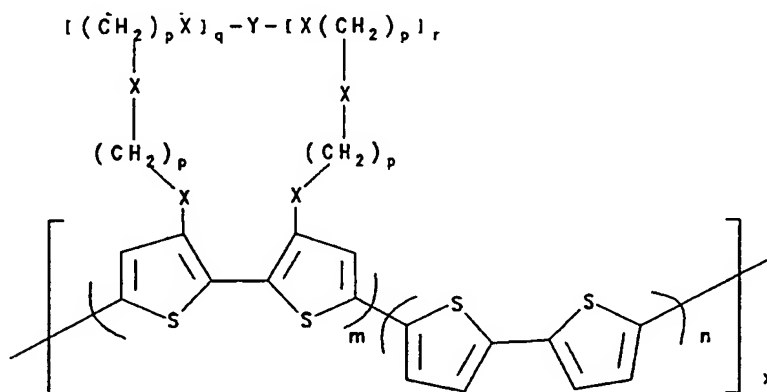


(3)

R_1 and R_2 are chosen to facilitate synthesis of the polythiophene compounds of the invention. It will be recognized, therefore, that R_1 and R_2 can be selected from a wide variety of groups known in the art. For example, R_1 and R_2 can be independently selected from H, Cl, Br, I, Li, $Sn(R_3)_3$, or $Si(R_3)_3$, although R_1 and R_2 preferably are the same.

Subscripts p likewise can be independently selected but preferably are the same. Preferably, p is 1 or 2.

In one preferred embodiment, bithiophene compounds having formula (2) are polymerized to produce polythiophene derivatives having formula (1):



wherein X , Y , R_3 , n , m , p , q , and r are as defined above. The polythiophene derivatives of the invention can include up to about 1000 monomeric units (i.e., x can be 1 to about 1000). Preferably, x is 1 to about 100, more preferably 1 to about 15.

The polythiophenes of invention can be substituted at one or more of the thiophene 4- or 4'-positions or other positions within the compounds of the invention. Such substitutions may be desirable, for example, to influence the electronic properties of the polymeric chain either directly or to introduce steric constraints. Due to steric constraints, substitution with relatively small groups (e.g., fluoro and methyl groups) are believed to be preferred. Such substitutions are envisioned to provide inductive effects, modifying the local electronic structure of the polythiophene chain. The optimal substituent for a given stimulus can be determined by routine experimentation. It also may be desirable to introduce slightly larger groups (e.g., ethyl groups) as substituents on the polythiophene chain to introduce additional steric constraints for control either the planarity of the polythiophene chain in the absence of a chemical stimulus or the ability of the chain to rotate out of plane in response to stimulus binding.

It will also be appreciated that each thiophene unit in the polythiophene derivatives of the invention need not bear a macrocyclic moiety. Indeed, it may prove desirable to incorporate into the polymeric chain thiophene units having no macrocyclic component.

As will be recognized, compounds having formulas (1) and (2) include two general structural components: a thiophene moiety (e.g., a thiophene unit or covalently bound thiophene units) and a macrocyclic moiety (i.e., an exocyclic tether joining the different thiophene positions). Macrocyclic moieties preferably span the 3 and 3' positions of a bithiophenic monomer of the invention, but also may span other positions of the same or different thiophene units. In terms of ion selectivity, it appears that polythiophene derivatives having relatively smaller macrocyclic moieties generally give the largest response for relatively small ions such as Na⁺ and that polythiophene derivatives having larger macrocyclic moieties generally are more sensitive for larger ion such as K⁺.

In the polythiophene derivatives of the invention the macrocyclic moieties are believed to bind or chelate specific chemical species to be detected and, thereby, induce a change in the local electronic structure of the polythiophene derivative of formula (1) or (2). This is believed to be accompanied by a decrease in pi-orbital overlap between thiophene rings and, hence, a decrease in the extent of conjugation. Also, when $X = O$ the ability of the oxygens at the 3-position to donate electron density into the polymer backbone appears to be limited due to lone pair electron interactions with the bound chemical species. Both effects result in a hypsochromic shift and an increase in the band gap of the polymer. Moreover, stimulus (M^+) binding is believed to induce a conformational change wherein the polythiophene chain changes from a planar conformation to a twisted conformation, as is shown in Figure 1 for polythiophene species wherein X is O or $-CH_2-O-$, and z is 1 or 2. Such twisting of the chains is believed to disrupt the electrical conductivity of the polymer. Any change in conductivity is detected and translated into changes in the concentration of the stimulus.

Twisting of the polymer's backbone from planarity also is believed to reduce its effective conjugation length. Accordingly, the polymers of the invention exhibit large ionochromic responses which are easily detected visually.

Sensing devices also are provided in accordance with the invention. The term sensor or sensing device, when used in the context of the invention, refers to devices that are capable of producing measurable, steady-state responses to one or more stimuli of interest.

Figure 2 shows a sensing device according to the invention wherein a layer 20 containing a polythiophene derivative is disposed on an insulating substrate 22. The substrate bears on its surface at least two contacts 24 that are in electrical communication with one another. Interposed between the contacts and in electrical communication therewith is a suitable means 26 for measuring resistance. Those skilled in the art will appreciate that the spirit of the invention may

be implemented in different forms. Typically, the resistance of the polythiophene is monitored as the observed signal either by measuring the current with a fixed voltage drop across the polymer or by measuring a voltage drop with fixed current. As
5 will be recognized, such devices can be employed in series or in parallel with other sensors or electronic elements. Upon binding of a specific stimulus by the macrocyclic moieties of the polymer, either a conformational change, or, depending upon which polymer is used, an inductive electronic effect is
10 introduced into the polymer backbone. Consequently, the conductivity of the polymer changes and this is detected as either a change in current or a change in voltage across the electrical contacts.

The sensors of the present invention find use in the
15 medical arts in, for example, the monitoring of electrolyte concentrations of bodily fluids. Such sensors also can be used to detect ions or organic molecules which may be present in the form of contaminants and, thus, will find use in the manufacturing and quality control fields. The sensors of the
20 invention also can be used for other applications such as, for example, in the monitoring of chemical processes.

The polythiophene-based sensors of the invention can be constructed to detect a wide variety of different stimuli. The only requirement for such sensors is that the macrocyclic
25 component of the polythiophene induce a conformational change or electronic perturbation in the polythiophene backbone upon binding a stimulus of interest. Useful macrocyclic components preferably include crown ethers. As will be recognized, the specificities crown ethers for many chemical species are well
30 known in the art. See, e.g., Hiraoka, Crown Compounds: Their Characteristics and Applications, Elsevier Sci. Pub., 1982. The invention, however, is not limited to compounds containing crown ether macrocyclic components, but includes compounds having any macrocyclic components set forth above that binds a
35 stimulus of interest and thereby effects a conformational change, an inductive electronic perturbation to the polythiophene backbone, or a reduction/oxidation (redox)

process. The term polythiophene backbone, when used in connection with the present invention refers to a polymeric network of thiophene molecules covalently bound to one another at 2 and 2' positions.

5 The polythiophene derivatives of the invention generally can be prepared by methods known in the art, including electrochemical oxidation, chemical oxidation, and chemical coupling reactions. Figure 3 shows a number of exemplary syntheses. Two routes to monomer 4 were investigated
10 utilizing copper catalyzed alkoxylation to directly attach the terminal oxygens of a polyether tether to the 3-positions of thiophene rings. The first involves alkoxyating 1 ($a = \text{CuOCH}_2-(\text{CH}_2\text{OCH}_2)_{n+2}-\text{CHOCu}$, t-butanol, lutidine, 80°C) and then forming bithiophene containing macrocycle by selectively
15 coupling 2 at its 2,2'-thiophene positions. The second involves alkoxyating 3 (formed by the reaction of 2,2',5,5'-tetrabromobithiophene under conditions d, i.e., Zn, HOAc, n-propanol, reflux in 50% yield) to form the macrocycle directly (yield 3→4 9.3%). The latter route gives variable low yields
20 and the major product is bithiophene, showing that reductive dehalogenation predominates under these conditions. The former proceeds smoothly to give 2 ($z=1$, $z=2$) in 33% and 36% yields, respectively. Treatment of the dilithio species of 2 in dimethyl ether with copper (II) chloride ($b = 2$ eq. BuLi, DME,
25 0°C ; $c = \text{CuCl}_2$, DME, room temperature) gave the desired macrocycle 4 in approximately 20% yield.

Polymer 6 was prepared by a method whereby dilithiated monomer 5 is formed and then refluxed in THF with $\text{Fe}(\text{acac})_3$. In this $\text{Fe}(\text{III})$ polymerization, insoluble $\text{Fe}(\text{acac})_2$ is
30 separated by filtration to produce materials free of the iron salts which typically plague FeCl_3 oxidative polymerizations. Additionally, ^1H NMR showed no evidence of the deleterious α - β coupling which is usually observed in oxidative polymerizations of thiophenes. After precipitating 6 in methanol, the degree
35 of polymerization of the soluble (i.e., low molecular weight) portion was determined by ^1H NMR integration of the two

doublets resulting from the disubstituted thiophene end groups to contain ten thiophene units.

Figure 3 also shows the synthetic route to polythiophene derivatives 11 and 12, wherein methylene spacers are inserted between the polythiophene moiety and the macrocyclic moiety. 2-Bromo-3-methylthiophene is reacted with 0.5 eq Mg, 0.5% NiCl₂dppp in diethylether at 0°C (yield = 98%). Subsequent reaction under conditions i, (2 eq. NBS in DMF/MeOH) followed by conditions j (NBS, benzoyl peroxide, AIBN in benzene at reflux) gives 2,2'-dibromo-4,4'-dimethoxymethyl bithiophene in 78% yield. Further reaction under conditions k (MOCH₂-(CH₂OCH₂)_{n,2}-CH₂OM for z=1, M=Na⁺, DME (55%); for z=2, M=K⁺, THF (18%)). The methylene spacers increase the size of the macrocyclic cavity and are believed to prevent electron donation from the macrocyclic moiety to the thiophene ring. As discussed below, only small responses are detectable for the compounds in which atoms X of the macrocyclic moiety are not connected directly to the polythiophene residues.

Stille coupling methodology also was used to prepared polythiophenes according to the invention. (See, Heck, Palladium Reagents in Organic Synthesis Academic Press, 1985; Stille, *Angew. Chem. Int. Ed. Engl.* 1986, 25, 508.) In this case, the dilithio species of 5 and 10 are reacted *in situ* with trimethyltin chloride and then subjected to palladium catalyzed cross-coupling (PdCl₂(AsPh₃)₂) with 5,5'-dibromo-2,2'-bithiophene. The molecular weights produced in this procedure were most likely solubility limited since these copolymers precipitated during the course of the reaction. The molecular weights as determined by GPC relative to polystyrene standards were determined to be 2800, 3700, 2000, and 1900 for polymers 7, 8, 11, and 12 respectively. However, the absolute molecular weights may be higher since the absolute molecular weight determined by NMR end group analysis for 6 shows the true molecular weight (1800) to be almost double that determined by GPC (960).

The relative association constants of compounds having formula (2) were measured for K⁺, Na⁺, and Li⁺ using standard

picrate extraction techniques generally in accordance with Koenig, et al., *J. Am. Chem. Soc.* 1979, 101, 3553. For comparative purposes, the association energies for 18-crown-6 also were measured. The binding constants for all monomers 5 were on the order of 10^3 times lower than that observed for K^+ with 18-crown-6. Monomer 4 bound approximately twice as effectively as the methylene spaced monomer 9.

Ionochromic effects were measured in 0.1M salt solutions in acetonitrile and the results are shown in Table 1. 10 Polymers 6, 7, and 8 show large shifts in λ_{max} with the appropriate ion. Because these shifts occur in the visible region, dramatic color changes are observed. As anticipated, polymers 6 and 7 show the largest shift for sodium, and 8 is most responsive to potassium. The large magnitude of the shift 15 despite the low binding constants for the corresponding monomers likely is attributable to the additive effect of destroying conjugation at several points along a highly conjugated system. This is supported by the fact that copolymer 7, in which the number of twisting sights has been 20 reduced, shows a smaller shift than its corresponding homopolymer, 6. The poor ionochromic activity of polymers 11 and 12 is not surprising considering their poor binding affinity (which results in failure of the twist-inducing mechanism) and the loss of electrostatic interaction between 25 the terminal oxygens of the polyether tether and polymer backbone.

Table 1

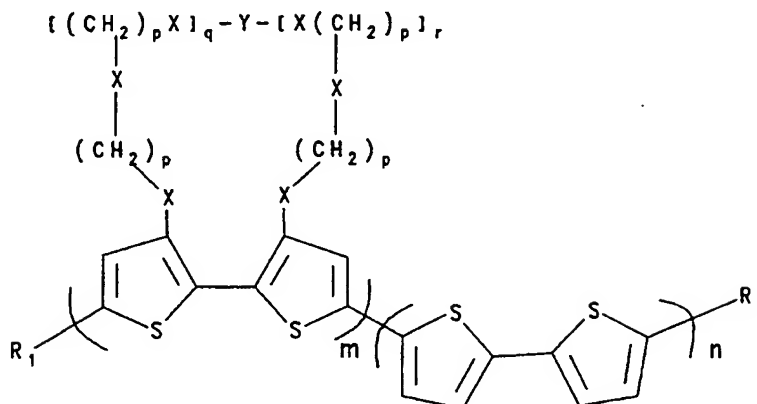
Polymer	λ_{max} (nm)	K^+	Na^+	Li^+
30 <u>6</u>	497	22	91	46
<u>7</u>	510	10	63	15
<u>8</u>	524	45	30	13
<u>11</u>	434	-4	3	3
<u>12</u>	432	1	3	4

Those skilled in the art will appreciate that numerous 35 changes and modifications may be made to the preferred embodiments of the invention and that such changes and

modifications may be made without departing from the spirit of the invention. For example, by the implementation of known molecular recognition principles, the compounds disclosed herein can be modified to produce conducting polymers which are
5 responsive to numerous chemical entities. It is therefore intended that the appended claims cover all such equivalent variations as fall within the true spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A compound having formula:



wherein:

R_1 and R_2 are, independently, H, Cl, Br, I, Li, $Sn(R_3)_3$, or $Si(R_3)_3$;

X is O, NR_3 , or S;

Y is $(CH_2)_p$, aryl having 6 to about 14 carbon atoms, or calixarenyl having 18 to about 200 carbon atoms;;

R_3 is alkyl having 1 to about 5 carbon atoms;

m is 1;

n is 0 or 1;

each p is, independently, 1 to about 5;

q is, independently, 0 to about 5; and

r is, independently, 0 to about 5.

2. The compound of claim 1 wherein each X is O.

3. The compound of claim 1 wherein each X is S.

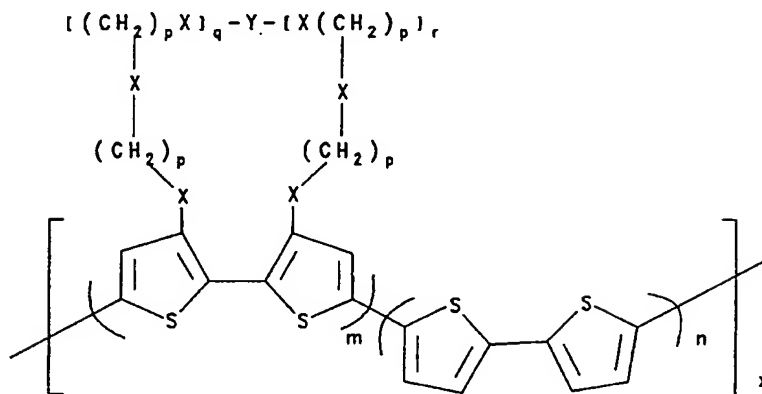
4. The compound of claim 1 wherein each X is NR_3 .

5. The compound of claim 1 wherein Y is $(CH_2)_2$.

6. The compound of claim 1 wherein Y is phenyl.

7. The compound of claim 1 wherein R_1 and R_2 both are H, Br, or Li

8. A compound having formula:



wherein:

X is O, NR_3 , or S;

Y is $(CH_2)_p$, aryl having 6 to about 14 carbon atoms, or calixarenyl having 18 to about 200 carbon atoms;;

R_3 is alkyl having 1 to about 5 carbon atoms;

each m is, independently, 1 to about 5;

each n is, independently, 0 to about 5;

each p is, independently, 1 to about 5;

each q is, independently, 0 to about 5;

each r is, independently, 0 to about 5; and

x is 1 to about 1000.

9. The compound of claim 8 wherein each X is O.

10. The compound of claim 8 wherein each X is S.

11. The compound of claim 8 wherein each X is NR_3 .

12. The compound of claim 8 wherein m is 1 and n is 0.

13. The compound of claim 8 wherein n is 1 and m is 1.

17

14. The compound of claim 8 wherein x is 1 to about 15.

15. The compound of claim 8 wherein p is 2.

16. The compound of claim 8 wherein q is 1.

17. The compound of claim 8 wherein r is 0.

18. The compound of claim 1 wherein Y is $(\text{CH}_2)_2$.

19. The compound of claim 1 wherein Y is phenyl.

20. A sensor comprising a substrate and at least one layer on said substrate, said layer including at least one compound according to claim 8.

21. The sensor of claim 20 further comprising means for determining conductivity for said layer.

22. A process for preparing a sensor comprising the steps of providing a substrate and placing upon said substrate at least one layer that includes at least one compound according to claim 8.

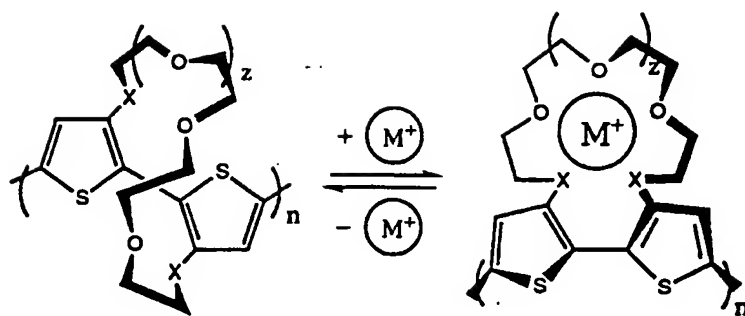


Figure 1

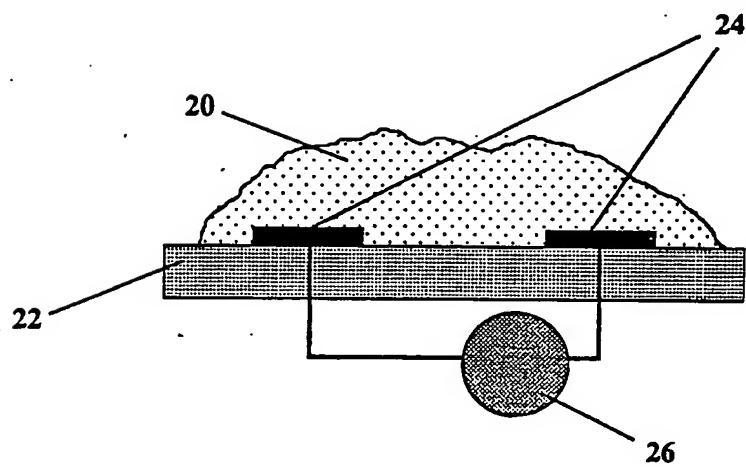


Figure 2

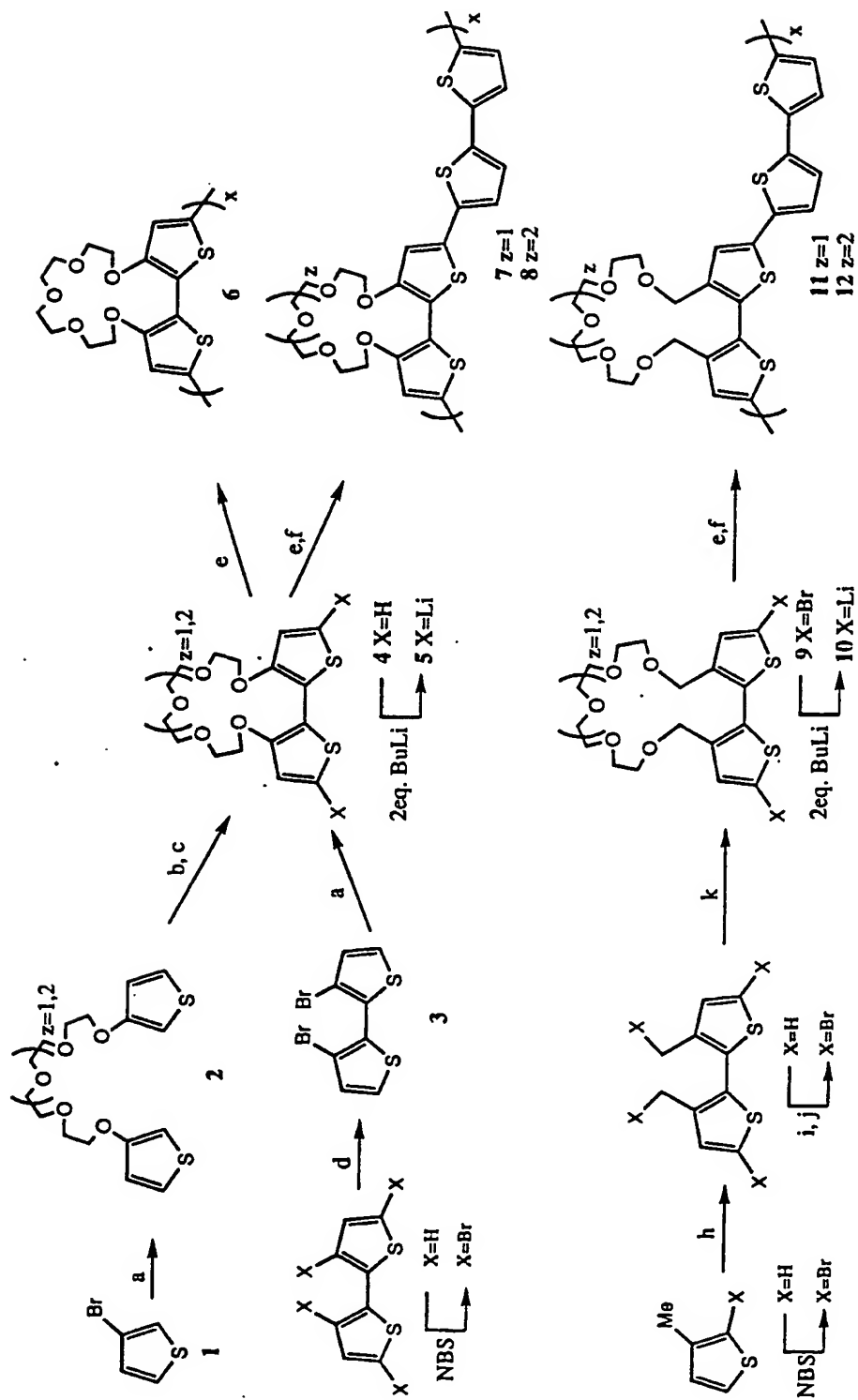


Figure 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/14658

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C07D 333/26, 333/32, 333/34, 333/36, 409/04

US CL : 549/4, 59, 62, 63, 68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 549/4, 59, 62, 63, 68

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,438,251 (HERWEH) 20 MARCH 1984, column 1, lines 15-17, 25-26; column 2, lines 20-25.	1-22
Y	US, A, 4,699,966 (HARRIS ET AL) 13 OCTOBER 1987, columns 5 and 6.	1-22
Y	US, A, 4,992,559 (KATHIRGAMANATHAN ET AL) 12 FEBRUARY 1991, see abstract; column 1, lines 29,44; column 3, lines 21-27; column 4, lines 65-68.	1-22
Y	US, A, 5,200,041 (SIMONET ET AL) 06 APRIL 1993, column 1, lines 8-21; column 2, lines 5-10.	1-22
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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

•	Special categories of cited documents:	•T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

22 FEBRUARY 1995

Date of mailing of the international search report

24 MAR 1995

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/14658

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS SEARCH TERMS: CALIXARENE?, AZACROWN, THIAACROWN,
POLYTHIOPHENES, CROWN ETHERS

CAS ONLINE STRUCTURE SEARCH